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# Pressure-Induced $\delta$ to $\epsilon$ Phase Transformations in a Pu-Ga Alloy

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July 14, 2009

IXth US-Russian Workshop on the Fundamentals of Plutonium Science  
Pleasanton, CA, United States  
July 18, 2009 through July 20, 2009

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# Pressure-Induced $\delta$ to $\alpha'$ Phase Transformations in a Pu-Ga Alloy

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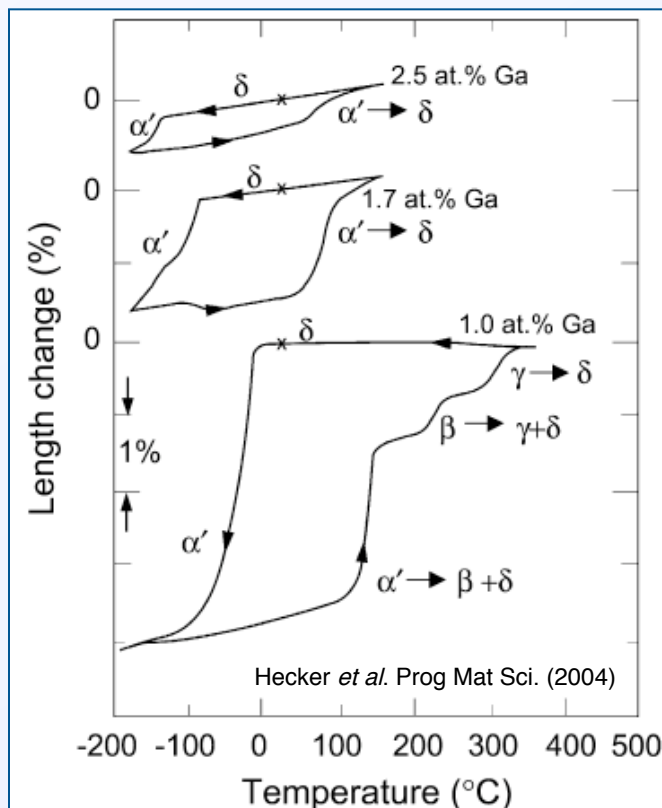
Lawrence Livermore National Laboratory, P. O. Box 808, Livermore, CA 94551

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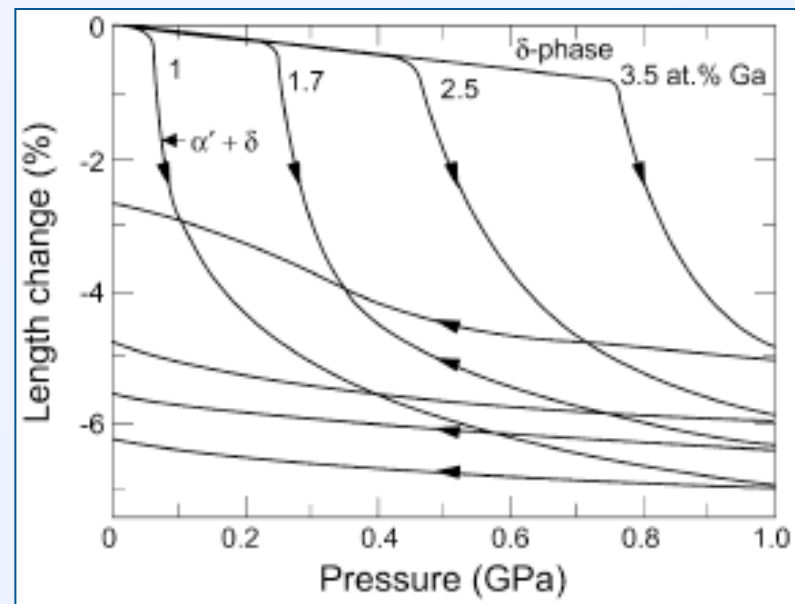
LLNL-CONF-xxxxxx

# Understanding the phase transformations remains as one of the significant Pu metallurgical challenges

The  $\delta \rightarrow \alpha'$  isothermal martensitic transformation can be induced with continuous cooling experiments



Under pressure, Pu - Ga alloys transform directly to  $\alpha'$  and undergo either a direct ( $\alpha' \rightarrow \delta$ ) or indirect ( $\alpha' \rightarrow \beta' + \delta \rightarrow \gamma' + \delta \rightarrow \delta$ ) reversion



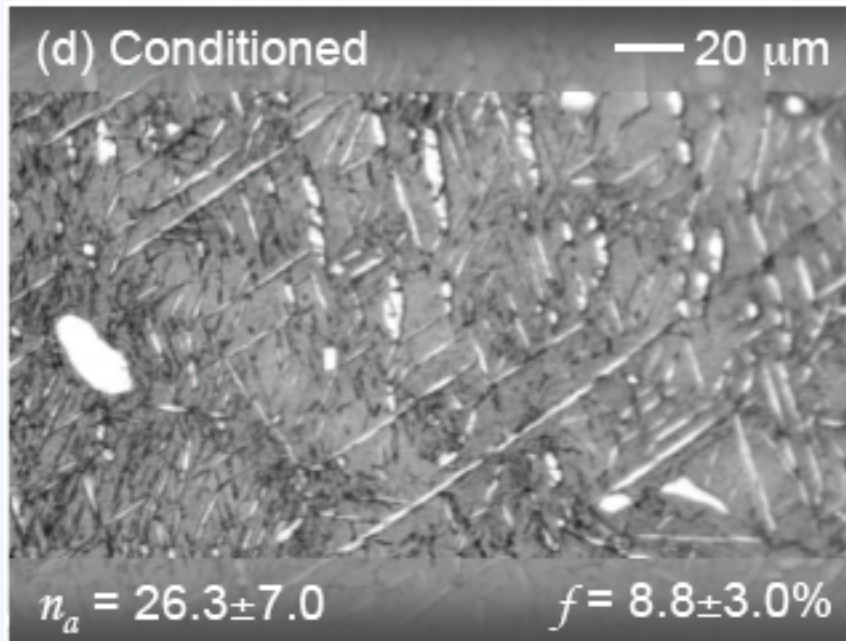


Low-temperature  $\delta \rightarrow \alpha'$  martensitic transformation

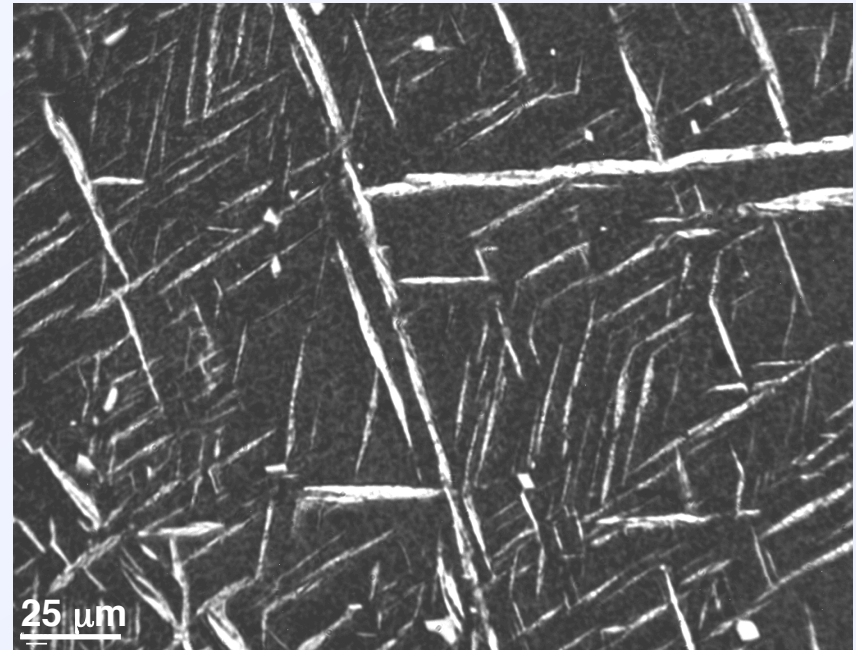
**The  $\alpha'$  particles that form from the isothermal martensitic transformation appear as lathes in optical microscopy**

Pu - 2.0 at.% Ga

-120°C/4 hours



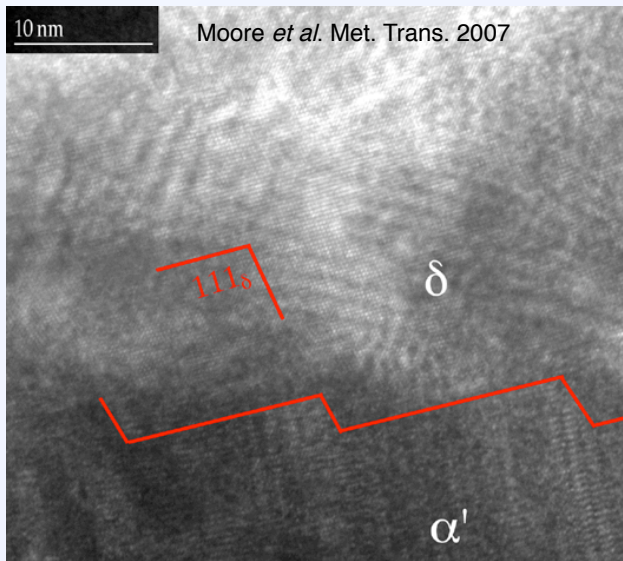
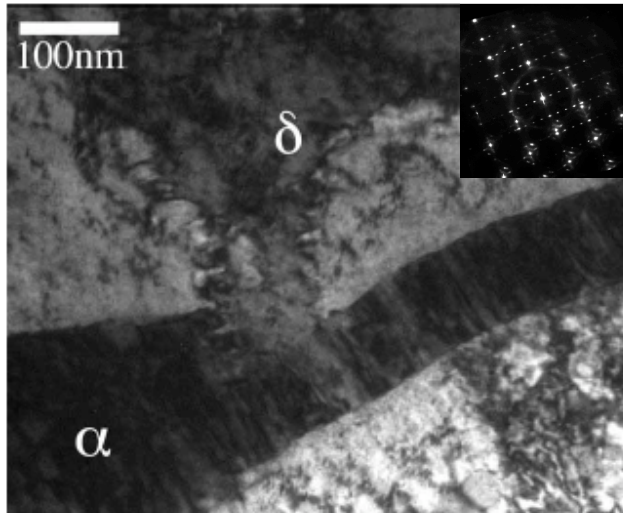
-155°C/4 hours



Partially transformed  
( $\delta + \alpha'$  phases)

**The  $\delta \rightarrow \alpha'$  isothermal martensitic transformation goes to  $\sim 25\%$  completion**

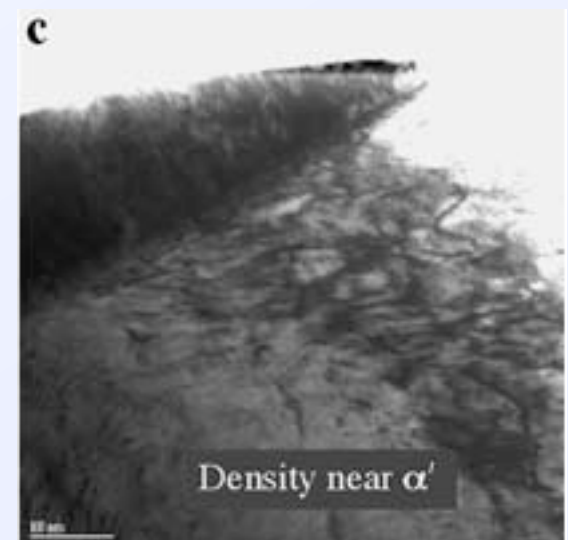
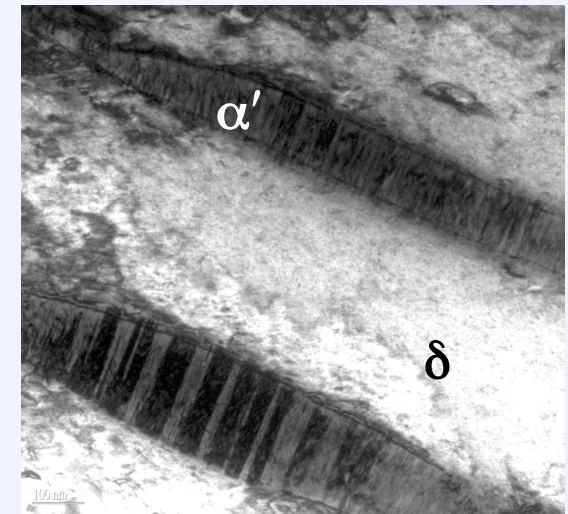
## The crystallography and morphology of the $\delta \rightarrow \alpha'$ transformation have been characterized with TEM



- The orientation relationship between  $\alpha'$  and  $\delta$  is:  
 $(111)_\delta \parallel (020)_{\alpha'}$   
 $[-110]_\delta \parallel [100]_{\alpha'}$

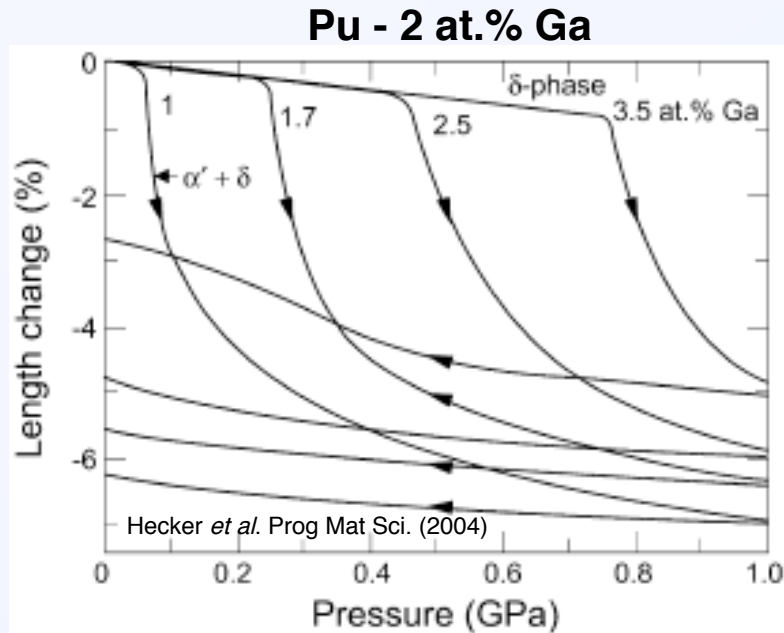
(Zocco *et al.* Acta Met. 1990)

- $\alpha'$  particles consist of 2 variants rotated  $60^\circ$  around  $\langle 020 \rangle_{\alpha'}$
- TEM shows  $(205)_{\alpha\beta}$  twinning as a lattice invariant deformation mode
- The  $\alpha'$ - $\delta$  interface is composed of a terrace and ledge structure that is faceted on  $111_\delta$
- The dislocation density is  $\sim$  an order of magnitude greater in the vicinity of  $\alpha'$  particles

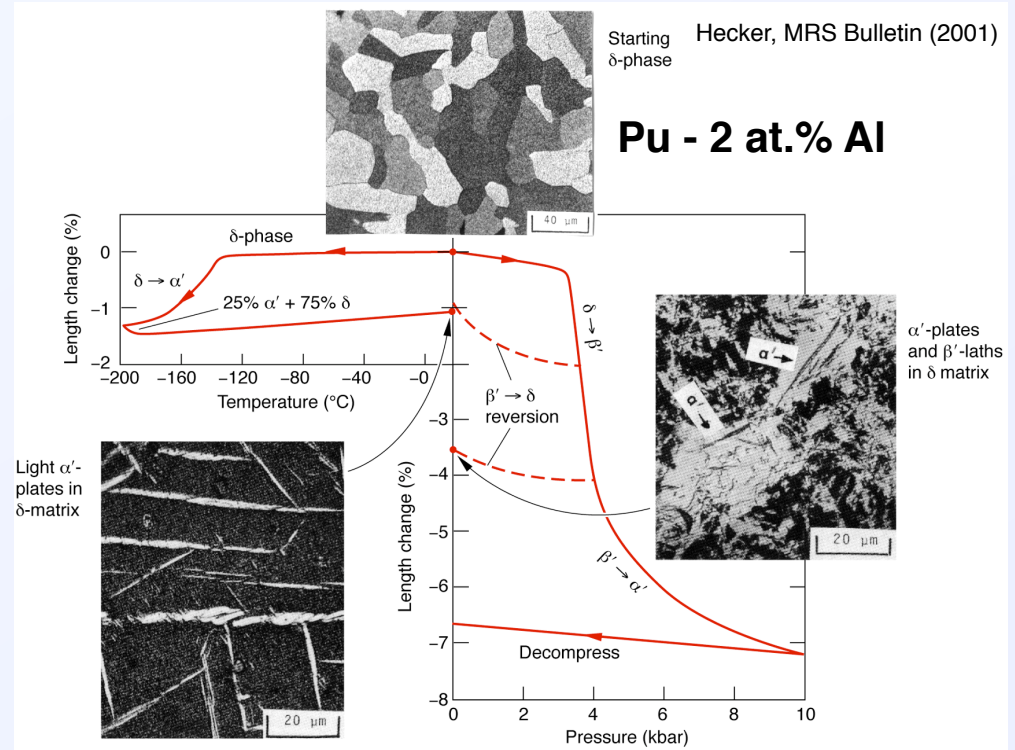


## Pressure-induced $\delta \rightarrow \alpha'$ martensitic transformation

# The $\delta \rightarrow \alpha'$ transformation can also be induced by pressure



- Under pressure, Pu - Ga alloys transform directly to  $\alpha'$  and undergo either a direct ( $\alpha' \rightarrow \delta$ ) or indirect ( $\alpha' \rightarrow \beta' + \delta \rightarrow \gamma' + \delta \rightarrow \delta$ ) reversion
- Reversion characteristics are similar to those in thermally-induced transformations



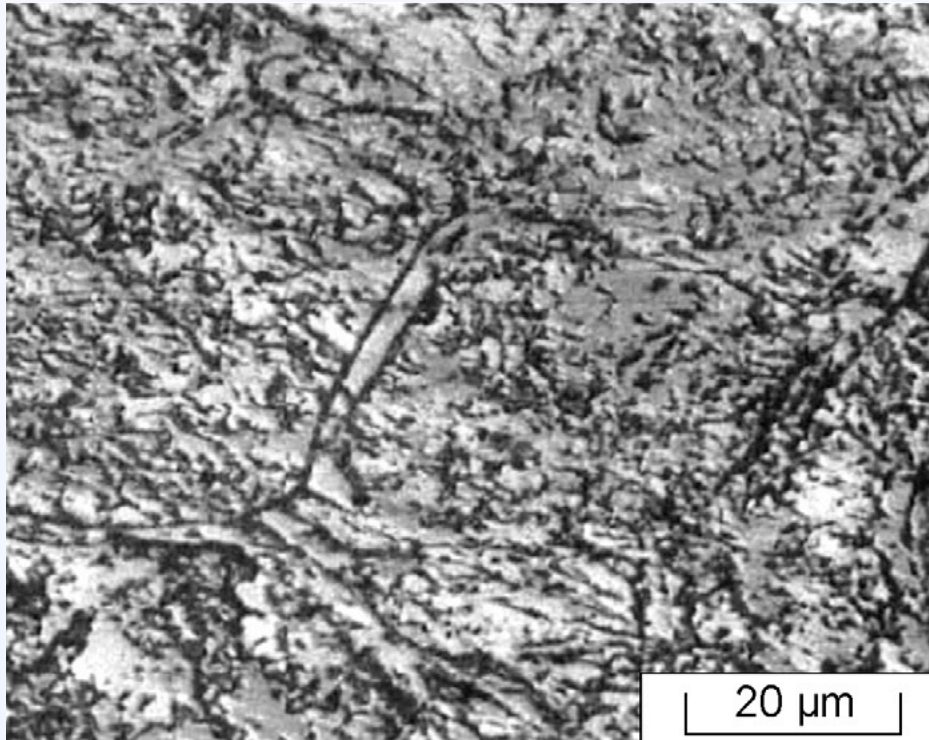
**Pu - 2 at.% Al alloy transforms first to  $\beta'$  then to  $\alpha'$  under pressure**



## Pressure-induced $\delta \rightarrow \alpha'$ transformation

**Upon cooling, Harbur reported that a 0.68 at.% Ga alloy has a density intermediate between  $\delta$  and  $\alpha$  phases**

Harbur, JALCOM (2007)



### After compressing to 1 GPa

Alloy	% $\alpha'$	% $\delta$	% amorphous
1.0 at.% Ga	87	0	13
1.7 at.% Ga	66	0	34
2.5 at.% Ga	68	12	20

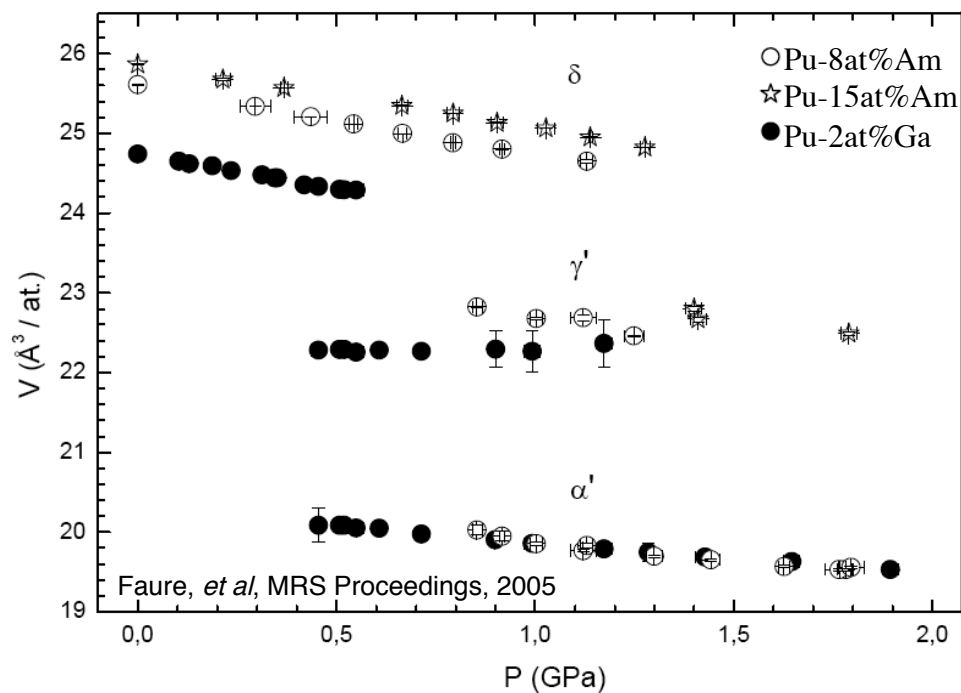
**Harbur proposes that the  $\delta$  phase transforms to  $\alpha'$  + amorphous phase**

- on cooling low solute alloys
- under pressure



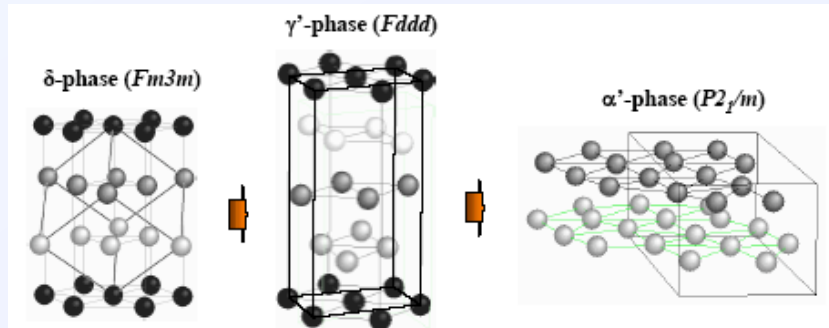
## Pressure-induced $\delta \rightarrow \alpha'$ transformation

# Diamond anvil cell experiments on a Pu - 2 at.% Ga alloy reveal $\delta \rightarrow \gamma' \rightarrow \alpha'$ transformation sequence



In the DAC, Pu - 2 at.% Ga transforms through the sequence  $\delta \rightarrow \gamma' \rightarrow \alpha'$

Zukas *et al.* (1981) report Pu - 2 at.% Al alloys transform through the sequence  $\delta \rightarrow \beta' \rightarrow \alpha'$

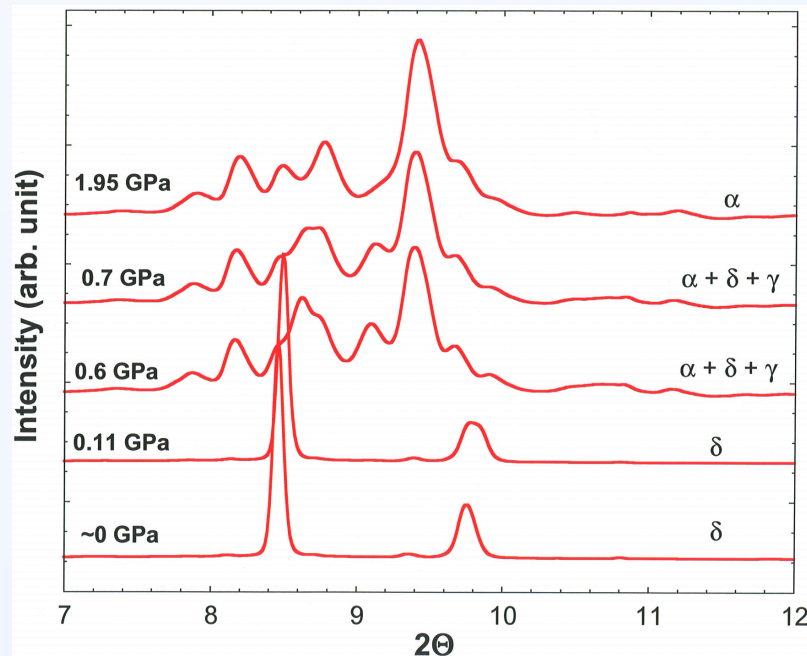


Faure *et al.* MRS Proceedings (2006)

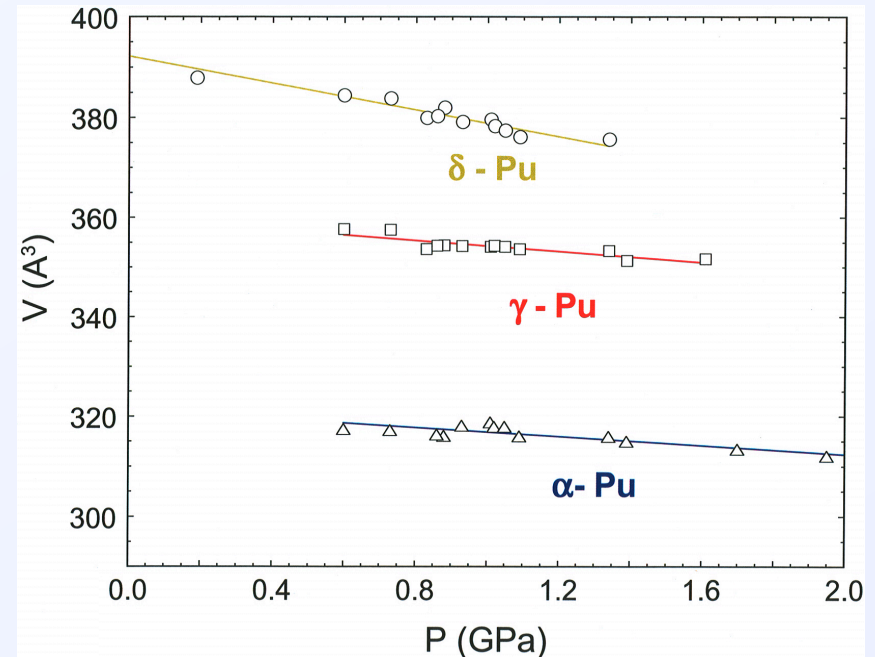


## Pressure-induced $\delta \rightarrow \alpha'$ martensitic transformation

Recent experiments at LLNL also suggest intermediate transitions between  $\delta$  and  $\alpha'$



- Diffraction peaks of the  $\delta$  phase split at low pressures to a  $\gamma'$  like structure
- $\gamma'$  like structure structure appears at  $\sim 0.6$  GPa

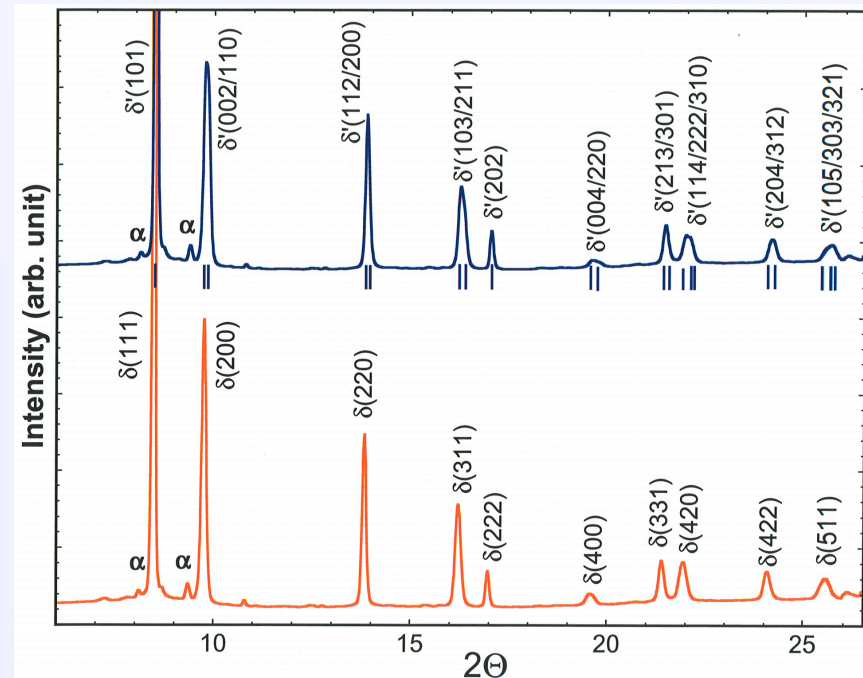


Schwartz *et al.* Prog Mat Sci. (2009)

- $\gamma'$  like structure structure disappears at  $\sim 1.6$  GPa

## At low pressure, $\delta$ phase distorts to $\delta'$

- Small amounts ( $< \sim 1\%$ ) of  $\gamma'$  and  $\alpha'$  coexist with  $\delta$  at ambient
- Is identified at  $\sim 0.1$  GPA
  - I4/mmm (S.G. 139,  $z = 2$ )
  - $a = 3.240 \text{ \AA}$
  - $c = 4.617 \text{ \AA}$
  - $V = 48.47 \text{ \AA}^3$  (0.2% denser than  $\delta$ -Pu)
  - Pressure induces growth of  $\gamma'$  and  $\alpha'$



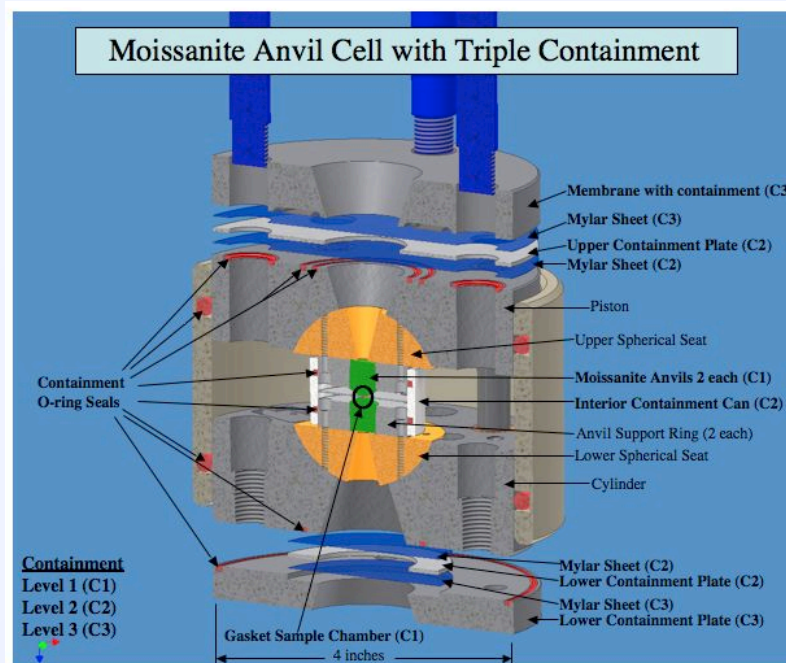
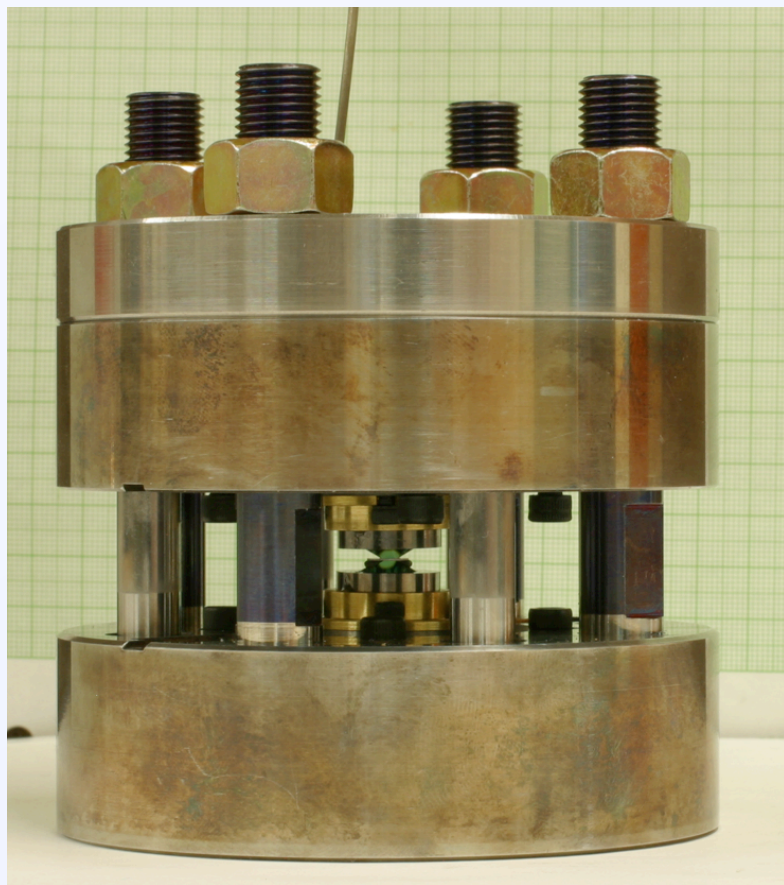
Schwartz *et al.* Prog Mat Sci. (2009)





Pressure-induced  $\delta \rightarrow \alpha'$  transformation

**We are coupling low pressure recovery experiments with TEM to elucidate the mechanism and morphology**

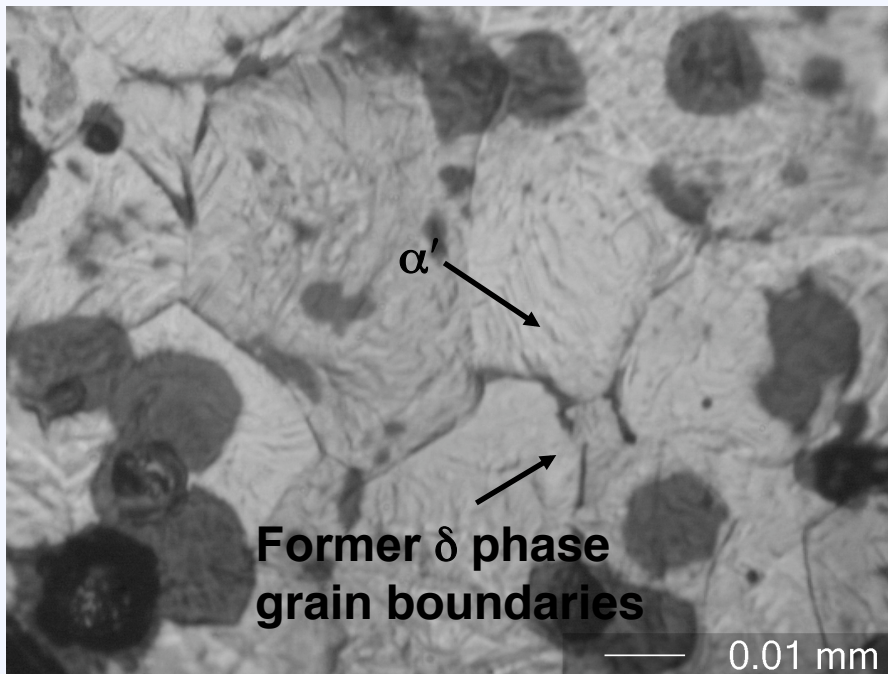


**2.3 mm diameter specimens are slowly compressed to 1 GPa in the large volume moissanite anvil cell**

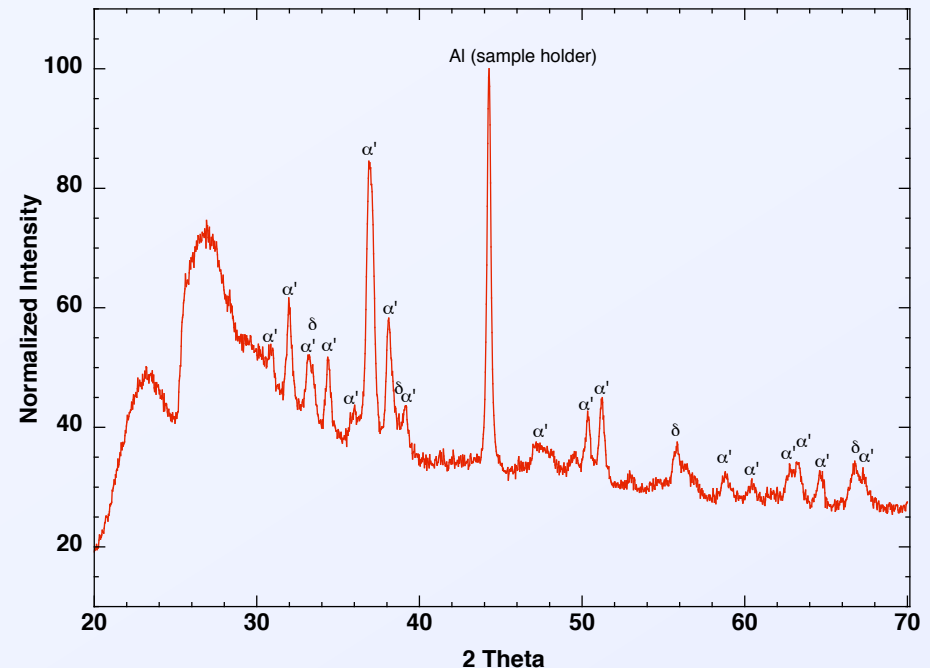




## Optical microscopy and x-ray diffraction of the compressed specimen reveals $\alpha'$ and $\delta$ phases



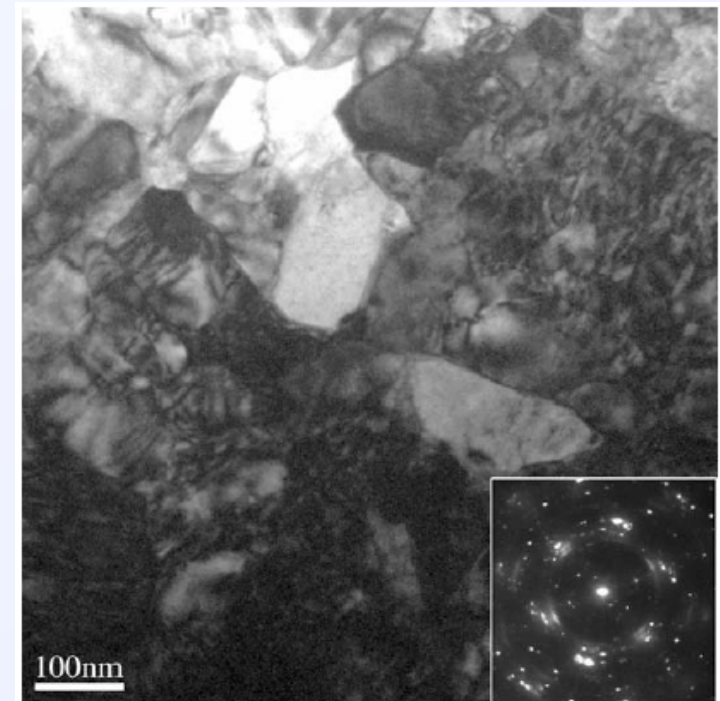
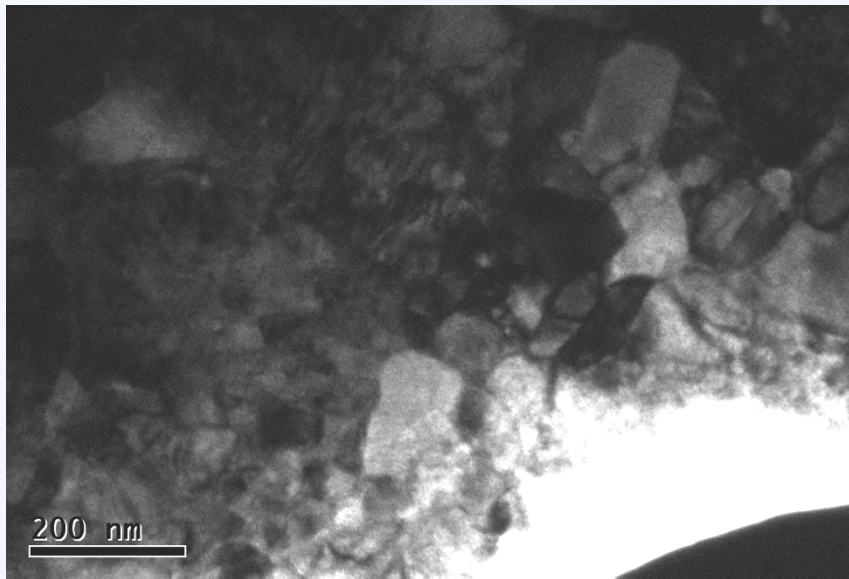
Optical microscopy does not have the resolution to differentiate between phases



X-ray diffraction experiments and simulations do not indicate the presence of an amorphous phase

Pressure-induced  $\delta \rightarrow \alpha'$  transformation

## The pressure-induced microstructure does not exhibit typical martensitic features



Pressure-induced  $\delta \rightarrow \alpha'$  transformation

Average  $\alpha'$  grain size  $\sim 100$ s nm, 10 – 20%  $\delta$

Implies nucleation-dominated mechanism

Low-temperature-induced  $\delta \rightarrow \alpha'$  isothermal martensitic transformation

Average  $\alpha'$  particle size  $\sim 1000$ s x 10,000s nm

Implies nucleation-limited mechanism (strain)

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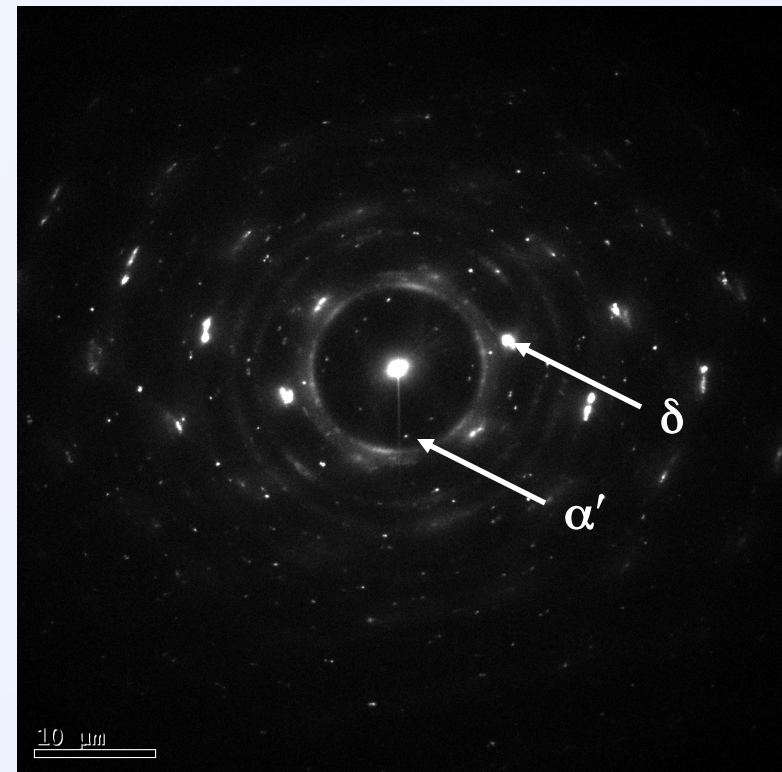
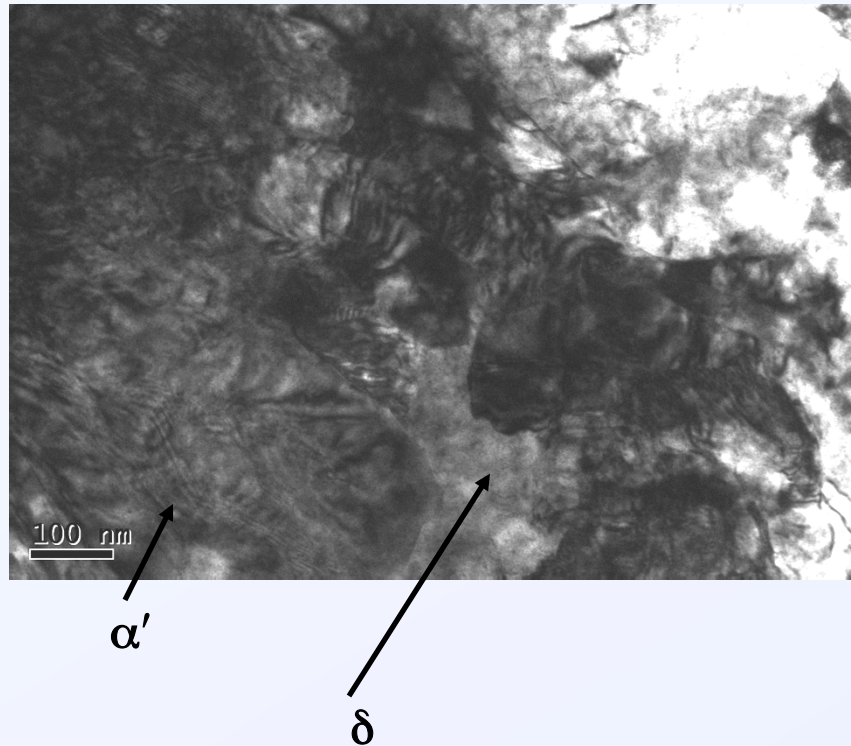
LLNL-CONF-404854

AJS Pu Futures - 08



Pressure-induced  $\delta \rightarrow \alpha'$  transformation

## Preliminary TEM reveals fine-grained $\alpha'$ and small amounts of $\delta$ – no evidence of an amorphous phase



**10 – 20%  $\delta$  phase is observed dispersed between the  $\alpha'$  grains**  
**High dislocation density**  
**No apparent orientation relationship (yet)**



# The isothermal martensitic and pressure-induced microstructures differ significantly

- Low temperature isothermal  $\delta \rightarrow \alpha'$  transformation
  - Nucleation is limited
  - Lath-shaped particles form
  - Intermediate phases are possible
- Pressure-induced  $\delta \rightarrow \alpha'$  transformation
  - Nucleation dominates
  - Very fine grain size results
  - No evidence of the amorphous phase
  - Intermediate phases are likely

